

PATENT

42261

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Masao SOMEYA et al.

Serial No.: 10/061,218

Filed: February 4, 2002

For: PROCESS FOR PRODUCING ALIGNED
CARBON NANOTUBE FILMS

Group Art Unit: 1754

Examiner: P. Lish

DECLARATION UNDER 37 C.F.R. § 1.132

We, Masao Someya and Takashi Fujii, hereby declare:

1. Masao Someya, received a master degree in Engineering from Tohoku University, Sendai, Japan in 1994. I have been employed by Mitsubishi Gas Chemical Company, Inc. since 1994, and have worked since 1994 in the Corporative Research Laboratory. Much of his research since 1994 has been devoted to Organic and Polymer synthesis, Catalytic chemistry, and Nanotechnology.

2. Takashi Fujii, received a Ph.D. degree from the University of Bristol, Bristol, UK, in 1998. He has been employed by Mitsubishi Gas Chemical Company, Inc. since 1991. He has worked in the Corporative Research Laboratory since 1991, except during the period of study at the University of Bristol. Much of his research since 1991 has been devoted to Organometallic chemistry, Catalytic chemistry, and Nanotechnology.

3. In order to compare the CNT film formed on the porous silica-alumina based substrate of our invention to those on a non-porous substrate, we conducted experiments using a flat and non-porous silicon wafer instead of a porous silica-alumina sheet.

In Comparative Example A, CNTs or carbon fibers were not obtained. Instead, only carbon particles were found. In Comparative Example B, bundles of aligned CNTs were obtained in places, but CNTs grew approximately in parallel with the surface, rather than the surface normal, on the major area of the surface. As a result, an aligned film failed to form.

Example A

This experiment corresponds to Example 3 of our above-captioned application, namely, a square silica-alumina substrate measuring 2 mm thick and 30 mm on each side was heated in air at 400°C for 3 hours and then deposited with aluminum by vacuum deposition. The deposited aluminum film was 0.2 μm thick.

An aqueous solution of cobalt nitrate (0.3 mol/L) was cooled to 10°C and to the stirred solution, 0.2 ml of 29% aqueous ammonia was added. Blue cobalt hydroxide particles were generated in the purple aqueous solution to form a suspension. After stirring the suspension for 10 minutes, the previously prepared aluminum-deposited substrate was dipped in the stirred suspension for 10 minutes.

The substrate was recovered from the suspension and calcined in air at 400°C for 3 hours.

After the calcining, the substrate was placed horizontally in a tubular quartz glass furnace (diameter is 35 mm) with the aluminum-deposited side facing up. The tubular furnace was heated up to 700°C with argon being blown horizontally at a flow rate of 360 cm^3/min under atmospheric pressure (0.1 MPa). Subsequently, with the temperature of 700°C being kept, a mixture of propylene (120 cm^3/min) and argon (360 cm^3/min) was introduced into the tubular furnace. After flowing of the propylene/argon mixed gas for 20

minutes, the gas supply was switched to argon and as argon was flowing, heating of the tubular furnace was stopped and it was left to cool to room temperature.

After the end of the reaction, the surface of the substrate was examined by SEM to confirm that an aligned carbon nanotube film was formed in a thickness of about 100 μm on the substrate.

Comparative Example A

For comparative purposes, a CNT film was prepared by the same procedure as in Example A, except that the porous silica-alumina sheet was replaced with a silicon wafer, and the aluminum deposition step was omitted. Thus, as a substrate, a square silicon wafer (Shinetsu Chemical plc. produced; phosphorus doped, n-type) measuring 30 mm on each side was prepared.

An aqueous solution of cobalt nitrate (0.3 mol/L) was cooled to 10°C. 0.2 ml of 29% aqueous ammonia was added to the solution with stirring. Blue cobalt hydroxide particles were generated in the purple aqueous solution, resulting in formation of a suspension. After stirring the suspension for 10 minutes, the silicon wafer above was dipped in the stirred suspension for 10 minutes.

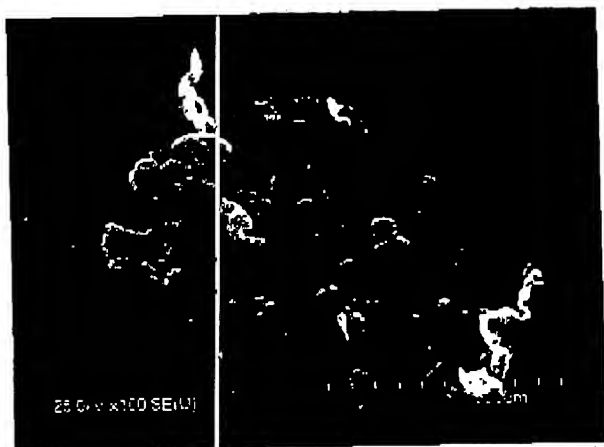
The substrate was withdrawn from the suspension and calcined in air at 400°C for 3 hours.

After calcining, the substrate was placed horizontally in a tubular quartz glass furnace (diameter 35 mm). The tubular furnace was heated up to 700°C with argon being blown horizontally at a flow rate of 360 cm^3/min under atmospheric pressure (0.1 MPa). Subsequently, with the temperature of 700°C being maintained, a mixture of propylene (120 cm^3/min) and argon (360 cm^3/min) was introduced into the tubular furnace, and was fed for 20 minutes. The gas supply was then switched to argon. Under the argon flow, the tubular furnace was allowed to cool to room temperature.

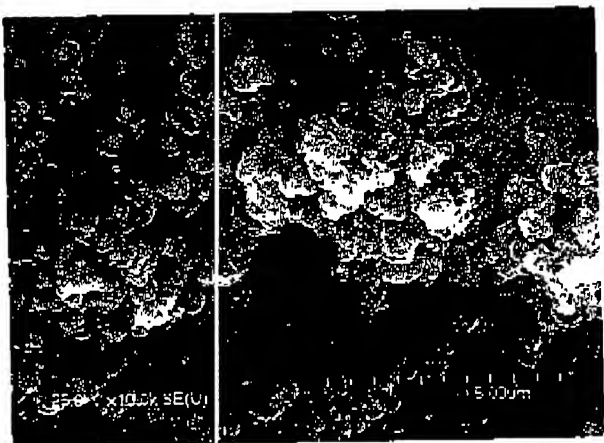
After the end of the reaction, the surface of the substrate was examined by SEM.

SEM image A shows that the clusters of carbon particles could be found sporadically on the

surface of the substrate. The carbon particles in the cluster had an external diameter of 20-100nm (SEM image B).



SEM image A The surface of the substrate (x100)



SEM image B The carbon particles (x10000)

Comparative Example B

For comparative purposes, a CNT film was prepared by the same procedure as in Example A, except that the porous silica-alumina sheet was replaced with a silicon wafer. Thus, as a substrate, a square silicon wafer (Shinetsu Chemical plc. produced; phosphorus doped, n-type) measuring 30 mm on each side was heated in air at 400°C for 3 hours and then

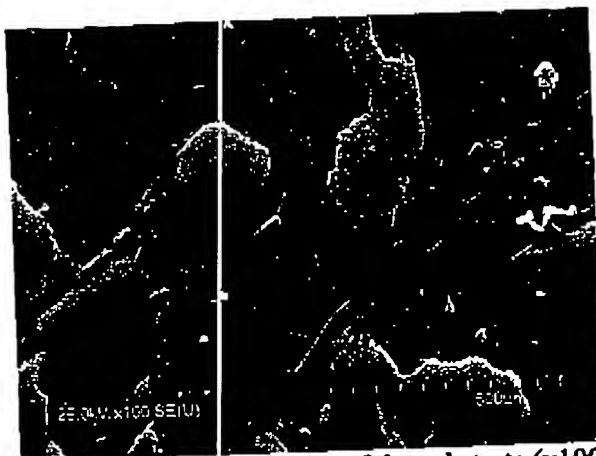
deposited with aluminum by vacuum deposition. The deposited aluminum film was 0.2 μm thick.

An aqueous solution of cobalt nitrate (0.3 mol/L) was cooled to 10°C and to the stirred solution, 0.2 ml of 29% aqueous ammonia was added. Blue cobalt hydroxide particles were generated in the purple aqueous solution to form a suspension. After stirring the suspension for 10 minutes, the previously prepared aluminum-deposited substrate was dipped in the stirred suspension for 10 minutes.

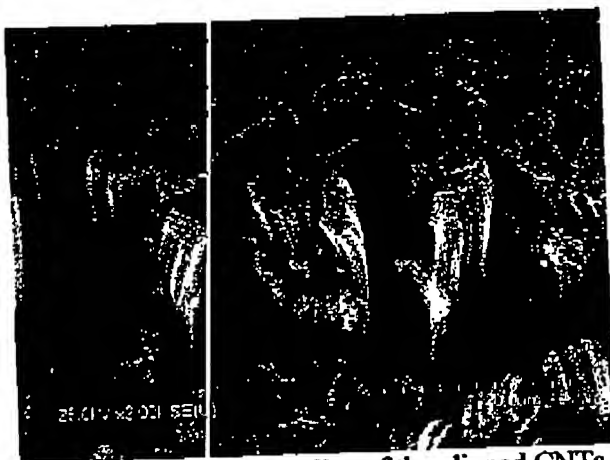
The substrate was recovered from the suspension and calcined in air at 400°C for 3 hours.

After the calcining, the substrate was placed horizontally in a tubular quartz glass furnace (diameter is 35 mm) with the aluminum-deposited side facing up. The tubular furnace was heated up to 700°C with argon being blown horizontally at a flow rate of 360 cm^3/min under atmospheric pressure (0.1 MPa). Subsequently, with the temperature of 700°C being kept, a mixture of propylene (120 cm^3/min) and argon (360 cm^3/min) was introduced into the tubular furnace. After flowing of the propylene/argon mixed gas for 20 minutes, the gas supply was switched to argon and as argon was flowing, heating of the tubular furnace was stopped and it was left to cool to room temperature.

After the end of the reaction, the surface of the substrate was examined by SEM. The appearance of the surface of the substrate was not uniform (SEM image C). On the minor area of the surface, there obtained aggregations of bundles of aligned CNTs, which were 10-60 μm high. The outside diameters of the bundles were 5-15 μm and there were 5-50 μm gaps in between those (SEM Image D). The CNTs forming the bundles had outside diameters of 5-15 nm and the density was as high as approximately 400 CNTs per 1 μm^2 . On the rest major area of the surface, CNTs grew but approximately in parallel with the surface, rather than the surface normal (SEM image E). On this area, the outside diameters of CNTs were 10-20 nm and the density was as high as 10 CNTs per 1 μm^2 .



SEM image C The surface of the substrate (x100)



SEM image D The bundles of the aligned CNTs (x2000)



SEM image E The CNTs in parallel with the surface (x10000)

4. In summary, an aligned CNT film was not produced on the silicon wafer. The porous silica-alumina sheet apparently retains the solution or suspension on the surface, and contributes to formation of the aligned CNT film.

5. In contrast, according to the process of the subject invention, CNTs grew vertically to form an aligned film as shown in Fig. 1 of the above-captioned specification. The thickness of the film was approximately 100 μ m, and the CNT forming the film had outside diameters of 5-8 nm, as described on page 12, lines 3-8 of the above-captioned specification. The thickness depends on the preparation conditions, and can exceed 100 μ m. On the basis of the SEM image of Fig. 1, the density of CNTs was as high as approximately 400 CNTs per 1 μ m².

6. We hereby declare further that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Masao Someya

Dated: October 25, 2004

Takashi Fujii

Dated: October 25, 2004